

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



## PATENT SPECIFICATION

NO DRAWINGS

1077.422

Date of Application and filing Complete Specification: Feb. 23, 1965.

No. 7802/65.

Application made in Japan (No. 9339) on Feb. 25, 1964.

Application made in Japan (No. 50652) on Sept. 8, 1964.

Complete Specification Published: July 26, 1967.

© Crown Copyright 1967.

Index at acceptance:—C3 F6X; C3 P(2A, 2C8B, 2C8C, 2C9, 2C10, 2C13A, 2C13B, 2C13C, 2C14A, 2C20B, 2D1A, 2K7, 4A, 4C8B, 4C8C, 4C9, 4C10, 4C13A, 4C13B, 4C13C, 4C14A, 4C20B, 4D1A, 4D3B1, 4K4, 4T2D, 4T2G, 4T2X, 7A, 7C8B, 7C8C, 7C9, 7C10, 7C13A, 7C13B, 7C13C, 7C14A, 7C20B, 7D2A1, 7K2, 8A, 8C8B, 8C8C, 8C9, 8C10, 8C13A, 8C13B, 8C13C, 8C14A, 8C20B, 8D2A)

Int. Cl.:—C 08 b 21/26 // C 08 f

## COMPLETE SPECIFICATION

## An improved Pigment Dispersion for Water Thinnable Paints

We, NIPPON PAINT CO. LTD., a Corporation organised under the Laws of Japan, of 1—1, Oyodomachi-Kita-2-chome, Oyodo-Ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pigment dispersions.

The invention provides pigment dispersions which are stable during storage and handling, and which afford improved pigment dispersibility when mixed with water-thinnable paints. The term "water-thinnable paints" as used herein means paints which contain latex emulsions or water-soluble resins as film-forming ingredients and which are to have their colour modified by the addition of pigment or more pigment.

Conventional pigment dispersions consist of pigments, surface-active agents and water as the main ingredients; they may also contain small proportions of other ingredients such as preservatives, anti-foaming agents and thickening agents. These pigment dispersions, except those containing large proportions of surface-active agents, are subject to aggregation of the pigment during storage or handling, and accordingly the use of such dispersions may be accompanied by defects such as unevenness of colour or lack of colour intensity. When these pigment dispersions are used for colour blending or toning the whole contents of the container of the dispersion is seldom used at once when the container is opened, and generally the remainder of the contents adheres to the walls of the container and at least partially

[Price 4s. 6d.]

dries out. When such a dried dispersion is mixed with a paint on a subsequent occasion, the resulting paint is not homogeneous because the dried out pigment forms lumps which are difficult to re-disperse or remove. Conventional pigment dispersions which contain large proportions of surface active agents in order to overcome the redispersibility problem are not easy to use satisfactorily. The present invention provides pigment dispersions having improved re-dispersibility even after drying out, and which are easy to use, so that the above mentioned disadvantages are avoided.

According to the present invention a pigment dispersion for blending with water-thinnable paints comprises a water-soluble hydroxyalkyl cellulose, or a water-soluble partially saponified polyvinyl acetate, or a water-soluble partially etherified derivative of such a partially saponified polyvinyl acetate or of a polyvinyl alcohol, to the extent of at least 5% preferably 10 to 30%, by weight (based on the weight of the pigment in the dispersion), and pigment.

The pigment may be incorporated in dry form or as a pre-formed conventional dispersion in an aqueous dispersion medium.

The present invention is applicable even to dispersions of inorganic pigments of the iron oxide series, such as red oxide and iron oxide yellow, or carbon black. The dispersibility into water-thinnable paints of these pigments in conventional pigment dispersions, especially those which have dried out, is generally poor. However, since these pigments are in practice excellent with regard to weather resistance and freedom from discolouration, inexpensive dispersions containing these pig-

ments and having improved dispersibility are desirable. The present invention has solved this problem.

5 Furthermore, conventional pigment dispersions which have been modified in conformity with the invention show improved pigment dispersibility during storage and handling.

10 Typical examples of thickening agents used in water-thinnable paints are polyvinyl alcohol, casein, methyl cellulose, CMC (sodium carboxymethyl cellulose), polyacrylates, and alginates. Hydroxyalkyl celluloses are also used for the same purpose. The proportion of thickening agent contained in the paint is 15 generally below 3 per cent by weight, usually 0.5 to 1.5 per cent by weight, based on the total pigments. The film-forming ingredients of such paints may be, for example, polyvinyl acetate, polyacrylates or polystyrene-butadiene.

20 The improved pigment dispersions of this invention are applicable without disadvantage to various kinds of water-thinnable paints, such as those indicated above, although, as in the case of Example 1, the effectiveness of the pigment dispersions varies with the type of the dispersion and the type of the paint.

25 The pigment dispersions of this invention contain the ingredients readily soluble in water in a suitable quantity compared with the pigments, and have a great tinting strength. The dispersions are usually employed in a proportion below 20 per cent by weight based on the original paint. For instance, a sufficient 30 degree of toning can usually be attained by adding the dispersion in a proportion below 10 per cent by weight to a white or other water-thinnable paint base.

35 Hydroxyalkyl celluloses which may be used in this invention include water-soluble cellulose derivatives produced by reaction of ethylene oxide or propylene oxide with cellulose, such as hydroxyethyl cellulose, hydroxyethyl hydroxypropyl cellulose and hydroxypropyl cellulose.

40 From the aspects of water solubility, pH and stability of viscosity of its aqueous solutions during storage and handling, hydroxyethyl cellulose is most suitable for the purpose of this invention among hydroxyalkyl celluloses. Particularly, these properties do not vary when the hydroxyethyl cellulose is used in the pigment dispersion and further contribute to the dispersion stability, toning properties and redispersibility after drying out.

45 Polyvinyl alcohols produced by complete saponification of polyvinyl acetates are unsuitable owing to their poor resolubility in aqueous liquids at room temperature.

50 In contradiction, in the present invention, there are used the polyvinyl alcohol derivatives formed by the partial saponification of polyvinyl acetates, and particularly, polyvinyl 55 alcohols or partially saponified products of

polyvinyl acetates, a proportion of the hydroxyl groups of which have been reacted with lower alkylene oxides, are preferably used. For example, hydroxyethyl etherified polyvinyl alcohols obtained by addition of ethylene oxide to polyvinyl alcohols show an increased hydrophilicity, and when the degree of etherification is above 10 percent based on the total hydroxyl groups, the polyvinyl alcohol etherified by ethylene oxide is readily soluble in water at room temperatures. 70 75

Water-soluble partially saponified polyvinyl acetate derivatives which may be used include those commercially available products having a saponification degree of approximately 80 to 90 percent. There may also be used hydroxyalkyletherified polyvinyl alcohols which are produced by reacting such lower alkylene oxides as ethylene oxide and propylene oxide with the above-mentioned partially saponified polyvinyl acetate or with polyvinyl alcohol obtained by complete saponification or with the condensation products of polyvinyl alcohol and carbonyl compounds. 80 85

As to the water-soluble hydroxyalkyl cellulose, a more detailed description will now be given. 90

Cellulose is a polysaccharide and its etherification is generally carried out in alkaline state. For instance, cellulose may be allowed to react with ethylene oxide, propylene oxide or ethylene chlorhydrin in the presence of alkali to give compounds having ethereal bonds between the said oxides and the hydroxyl groups of the glucose residues of cellulose, such as an ethylene glycol monoether bond, a propylene glycol monoether bond, a diethylene glycol monoether bond, a dipropylene glycol monoether bond, a polyethylene glycol monoether bond or polypropylene glycol-monoether bond. 95 100 105

Further, water-soluble cellulose derivatives such as hydroxyalkyl methyl cellulose and the alkali metal salts of hydroxyalkyl carboxymethyl celluloses, which are obtained by using methyl chloride, ethyl chloride or sodium chloroacetate together with ethylene oxide, propylene oxide or ethylene chlorhydrin in the aforementioned etherification reaction of cellulose, whereby some of the hydroxyl groups of the cellulose are substituted by methoxy, ethoxy or  $-\text{OCH}_2\text{COONa}$  radicals while others form ethereal bonds such as  $-\text{OCH}_2\text{CH}_2\text{OH}$  and  $-\text{OC}_3\text{H}_7\text{OH}$ , are included in the water-soluble cellulose derivatives which may be employed in this invention. 110 115 120

However, the advantageous effects of this invention decrease with increasing etherification of the cellulose derivatives by methyl chloride, ethyl chloride or sodium monochloroacetate, etc. This is probably because the celluloses etherified by ethylene oxide or propylene oxide and the like have stronger surface-active properties than those carrying methoxy or 125 130

ethoxy or like groups, and accordingly they provide a greater dispersing effect when they are used in the pigment dispersion.

In addition, it is believed that the alcoholic methylol radical ( $-\text{CH}_2\text{OH}$ ) contained in water-soluble hydroxyalkyl cellulose or hydroxyalkyl etherified polyvinyl alcohols, etc., when the pigment dispersion is used in conjunction with paints containing water-soluble resins having the N-methylol radicals on which produce N-methylol radicals on heating, such as N-methylol melamine resin derivatives, N-methylol urea resin derivatives and polymers containing N-methylol radicals, forms intermolecular bridge structures on heat treatment at a temperature of  $100^\circ$  to  $200^\circ$  C, whereby films of good water resistance and durability are formed.

Hydroxyalkyl celluloses employed in this invention are preferably completely dissolved in the pigment dispersion. A description will now be given taking commercial hydroxyethyl cellulose as an example. Hydroxyethyl celluloses of which a 2 per cent by weight aqueous solution has a viscosity above 1,000 cps. at a temperature of  $20^\circ$  C remain undissolved by the usual solution procedures under stirring and the swollen fine particles can be observed with the eye, some of which will not dissolve completely even stirred for many hours. Hydroxyethyl cellulose of which 2 per cent by weight aqueous solution has a viscosity below 30 cps. measured at a temperature of  $20^\circ$  C dissolves completely at the room temperature, no undissolved particles being observable. In addition, hydroxyethyl cellulose of lower viscosity is superior to that of higher viscosity in the dispersing effect towards pigments.

The requisite proportion of hydroxyalkyl cellulose (which may be an individual compound or a mixture of two or more different hydroxyalkyl celluloses) varies somewhat depending upon the kinds and proportions of the other ingredients of the pigment dispersion, but a proportion sufficient to cover the pigment particles is required, this proportion being at least 5 per cent by weight, preferably 10 to 30 per cent by weight, based on the pigments. It is preferred to employ hydroxyalkyl celluloses of which 2 per cent by weight aqueous solutions have a viscosity below 300 cps. measured at a temperature of  $20^\circ$  C.

The improved pigment dispersion which satisfies such conditions attains the primary objects when applied to paints. The residue adheres closely to the wall of container and gradually dries out, but is readily redispersed by stirring for a short time. Accordingly, the various defects resulting from drying out and aggregation as observed in the conventional pigment dispersions can be avoided.

The polyvinyl acetate or polyvinyl alcohol derivatives may be employed in a similar manner to the hydroxyalkyl celluloses. For

example, a 5% by weight aqueous solution of commercial polyvinyl alcohol having a degree of saponification of approximately 80 to 90 per cent shows a viscosity below 200 cps. measured at a temperature of  $20^\circ$  C. As in the case of hydroxyalkyl celluloses, those of which a 2 per cent by weight aqueous solution have a viscosity below 1,000 cps., preferably below 300 cps., measured at a temperature of  $20^\circ$  C, are adequate. In addition, it is desirable to add a small amount of a high boiling solvent as mentioned below in order to facilitate rapid redispersion. Such high-boiling solvents also are strikingly effective for retarding both the drying and solidification of the pigment dispersion in the course of manufacture or use.

Pigments which may be used in the dispersions of the invention may be of either the inorganic or organic types. Inorganic pigments include titanium dioxide, carbon black, cadmium red, red oxide and cadmium yellow; organic pigments include permanent red, Hanza yellow, phthalocyanine green and phthalocyanine blue. There may also be used "Colanyl" and "Pigmosol" pigments (products of Badische Anilin und Soda Fabrik Aktiengesellschaft), "EM Colour" (a product of Toyo Ink Manufacturing Co., Ltd.) and the pigments employed in conventional pigment dispersions such as the dispersed pastes for emulsion paints introduced by E.I. Du Pont de Nemours & Co.

Furthermore, fillers such as calcium carbonate, talc, clay, silica powder and mica powder may be used together with these pigment colours.

The surface active agent selected should be compatible with the dispersion and the paint with which the dispersion is to be used and should provide a stable dispersion of fine particles even at high pigment concentrations. Suitable surface active agents include the nonionic surface active agents such as polyoxyethylene alkyl ethers, polyoxyethylene aliphatic acid esters and polyoxyethylene alkyl phenol ethers, and anionic surface active agents such as sodium alkyl naphthalene sulphonates, sodium alkyl benzene sulphonates and high molecular polycarboxylic acids.

The dispersions may also contain water-miscible solvents of high boiling points, particularly, glycols and alkyl esters or alkyl ether derivatives thereof. For example, ethylene glycol, propylene glycol, polypropylene glycol, butylene glycol, hydroxyethyl acetate and butyl carbitol acetate can be used. In some of the conventional pigment dispersions with the object of reducing drying out during the storage and handling, such surface active agents or high-boiling solvents are used as the main constituent, but nevertheless residues sticking to the container walls and around the outlet dry out gradually, or a film forms on the surface, which makes redispersion difficult.

Also, the use of large proportions of surface active agent or high-boiling solvent is undesirable because it results in reduced wet abrasion resistance, alkali resistance and durability of the paints.

The invention is illustrated by the following examples. The amounts are parts by weight.

EXAMPLE 1.

To three samples each of 40 parts of a mixture (pigment content=50% by weight) of equal amounts of the five following commercial (conventional) pigment dispersions (each having a pigment content of about 40%—60% in aqueous medium),

- 1) "Permanent Red FGR Colanyl" (Heochst, West Germany)
- 2) "Permanent Yellow HR Colanyl" (Heochst)
- 3) "Heliogen Green GN Colanyl" (Badische, West Germany)
- 4) "Heliogen Blue B Colanyl" (Badische)
- 5) "Imperon Black K—BG Highly Conc." (Heochst)

were added, respectively, 50 parts of 5 per cent aqueous solutions of hydroxyethyl cellulose, methyl cellulose and CMC. To each sample were also added 5 parts of diethylene glycol and 5 parts of 10 per cent ( $\bar{p}=12$ ) of polyoxyethylene nonyl phenol ether. The obtained mixtures were stirred to uniformity and the resulting homogeneous mixtures are referred to as the sample dispersions. One sample of the mixture of conventional pigment dispersions, without additives, was used as a control. Tests were carried out on the sample dispersions and on the control by spreading them on glass plates in a thickness of 5 mils and then drying them in an oven at a temperature of 60° C for one hour, to dry them out. 2.5 parts of each original sample dispersion and control, and portions of each dried sample dispersion and dried control containing the same amount of pigment, were added to 100 part lots of white emulsion paints of usual commercial polyvinylacetate, polyacrylic, and polystyrene-butadiene types. The resulting mixtures were stirred with a glass rod for 10 minutes and then the toning property was assessed, giving the results illustrated in the following table.

lose, methyl cellulose and CMC. To each sample were also added 5 parts of diethylene glycol and 5 parts of 10 per cent ( $\bar{p}=12$ ) of polyoxyethylene nonyl phenol ether. The obtained mixtures were stirred to uniformity and the resulting homogeneous mixtures are referred to as the sample dispersions. One sample of the mixture of conventional pigment dispersions, without additives, was used as a control. Tests were carried out on the sample dispersions and on the control by spreading them on glass plates in a thickness of 5 mils and then drying them in an oven at a temperature of 60° C for one hour, to dry them out. 2.5 parts of each original sample dispersion and control, and portions of each dried sample dispersion and dried control containing the same amount of pigment, were added to 100 part lots of white emulsion paints of usual commercial polyvinylacetate, polyacrylic, and polystyrene-butadiene types. The resulting mixtures were stirred with a glass rod for 10 minutes and then the toning property was assessed, giving the results illustrated in the following table.

Table

Test results of toning property<sup>1)</sup>

Kind of Paint	Sample	Additives Test Item	Hydroxyethyl cellulose	Methyl cellulose	CMC	Control
Poly-vinyl acetate type	Sample dispersion	Colour uniformity	○ <sup>3)</sup>	X	○	○
		Touch up <sup>2)</sup>	○	X	X	△
		Strike	◎	◎	◎	◎
		Tinting strength	○	△	△	○
	Sample dried up	Colour uniformity	○	XX	○	XX
		Touch up	○	X	X	XX
		Strike	◎	XX	X	XX
		Tinting strength	○	△	X	XX
Poly-acrylic type	Sample dispersion	Colour uniformity	○	○	○	○
		Touch up	○	X	△	○
		Strike	◎	◎	◎	◎
		Tinting strength	◎	△	△	○
	Sample dried up	Colour uniformity	○	○	○	XX
		Touch up	○	X	X	XX
		Strike	◎	X	X	XX
		Tinting strength	○	X	△	XX
Poly-styrene butadiene type	Sample dispersion	Colour uniformity	○	○	○	○
		Touch up	△	△	△	X
		Strike	◎	◎	◎	◎
		Tinting strength	○	○	○	△
	Sample dried up	Colour uniformity	○	○	○	XX
		Touch up	△	X	△	XX
		Strike	○	X	△	XX
		Tinting strength	○	○	○	XX

- 1) Colour is near 7.5 P 7/2 when represented by Munsell's system.
- 2) This means the colour stripes which, in case of spreading with a brush, are produced along the course of the brush owing to the breakdown of the aggregated pigment masses by the shearing force of the brush.
- 3) Standard of assessment.

10 ○ : excellent;

○ : good;

Δ : usable limit;

X : practically inferior,

XX : practically unusable.

- 15 It will be observed that the sample dispersions containing methyl cellulose and CMC have some disadvantages for practical use with water-thinnable paints, whereas the sample dispersions employing hydroxyethyl cellulose are superior. There are very remarkable differences in the properties of the dried out samples, the worst being the control.

- 20 The samples containing methyl cellulose and CMC are considerably better than the control but they are still inadequate for practical use. On the other hand, the samples employing hydroxyethyl cellulose have excellent properties and are usable with each of the various kinds of water-thinnable paints even after being dried out. The proportions of hydroxyethyl cellulose used in this example are all 12.5 per cent based on the weights of the pigments in the sample dispersions.

#### EXAMPLE 2.

- 35 To 45 parts of "Imperon Black K—BG Highly Conc." (pigments, 40 per cent in an aqueous medium, Hoechst), 50 parts of 5 per cent aqueous hydroxyethyl cellulose solution (viscosity measured at 20° C: 150 cps.) were added, and blended by use of a stirrer so as not to bubble. To the obtained mixture, 5 parts of diethylene glycol were added and then the mixture was further stirred, whereby 40 100 parts of fluid pigment dispersion having a viscosity of approximately 80 K.U. (measured by use of Stormer's viscometer at a temperature of 20° C) were obtained. This dispersion can be used for toning various kinds of water-thinnable paints without difficulty and in particular the defects due to drying out are avoided. In this example, hydroxyethyl cellulose is used in a proportion of 13.9 per cent based on the weight of the pigments.

#### EXAMPLE 3.

- 55 A vibro-energy mill was charged with a mixture of 30 parts of "Tekka Red" (a product of Nippon Tekka Industry Co., Ltd.), 60 parts of 5 per cent aqueous hydroxyethyl cellulose solution (viscosity at a temperature of 20° C: 150 cps.), 0.5 part of "Demol EP" (an anionic surface active agent of high molecular polycarboxylic acid salts), 0.5 part

of polyoxyethylene nonyl phenol ether ( $\overline{p}=12$ ) and 9 parts of ethylene glycol and then was operated for 20 hours, whereby the desired pigment dispersion was obtained. In this case, the proportion of hydroxyethyl cellulose was 10 per cent based on the weight of the pigments.

A dispersion of similar properties is obtained even if the 9 parts of ethylene glycol are omitted.

#### EXAMPLE 4.

To 30 parts of "Imperon Yellow KR Extra Conc." (pigment, approximately 50 per cent in an aqueous medium; Hoechst), 65 parts of a 5 per cent (by weight) aqueous solution of partially saponified polyvinyl acetate (degree of polymerization: ca. 600; degree of saponification: 88 per cent) and 5 parts of diethylene glycol were added and mixed well. The obtained pigment dispersion readily dispersed into various kinds of water-thinnable paints even after drying out, and its stability after three months' storage was excellent.

The proportion of partially saponified polyvinyl acetate used in this example is about 22 per cent based on the weight of the pigments.

#### EXAMPLE 5.

To each of 40 part lots of "Tekka Red" and of "Tekka Yellow" (iron oxide series inorganic pigments, products of Nippon Tekka Industry Co. Ltd.) respectively, in pot mills, 54 parts of a 10 per cent aqueous solution of hydroxyethyl etherified polyvinyl alcohol (degree of polymerization: ca. 1,000; degree of saponification: 99 per cent; etherification degree: 15 per cent), 5 parts of diethylene glycol, and one part of 25 per cent aqueous solution of dispersing agent (sodium polycarboxylate) were added; and then the mills were operated for 16 hours to provide pigment dispersions of reddish brick-colour and yellow ochre colour, respectively. In this example, the proportion of hydroxyethyl etherified polyvinyl alcohol used is 13.5 per cent based on the weight of the pigments.

To the pigment dispersions of this invention, other additives such as emulsions or water-soluble resins, antifoaming agents and preservatives may be added provided they do not adversely affect the desired properties. Examples of suitable antifoaming agents are "Nopco" (a product of Nopco Chemical Company), "Balab bubble breaker" (a product of Balab Co.) and tributyl phosphate. Examples of suitable preservatives are "Monin" (a product of Takeda Chemical Industries, Ltd.) and "Molden" (a product of Nagase & Co., Ltd.).

#### WHAT WE CLAIM IS:—

1. A pigment dispersion for blending with water-thinnable paints, comprising, as essential ingredients, a water-soluble hydroxyalkyl cellulose, or a water-soluble partially saponi-

- 5   fied polyvinyl acetate, or a water-soluble partially etherified derivative of such a partially saponified polyvinyl acetate or of a polyvinyl alcohol, to the extent of at least 5% by weight (based on the weight of the pigment in the dispersion), and pigment.
- 10   2. A pigment dispersion as claimed in claim 1 wherein water-soluble hydroxyethyl cellulose is employed as the water-soluble hydroxyalkyl cellulose.
- 15   3. A pigment dispersion as claimed in claim 1 wherein a water-soluble hydroxyalkyl cellulose, of which a 2 percent aqueous solution has a viscosity below 300 cps. at a temperature of 20° C, is employed.
- 20   4. A pigment dispersion as claimed in claim 1 wherein the water-soluble partially saponified polyvinyl acetate is a polyvinyl alcohol having a saponification degree of 80 to 90%.
- 25   5. A pigment dispersion as claimed in any of the preceding claims wherein the pigment is carbon black or iron oxide.
- 30   6. A pigment dispersion as claimed in any of the preceding claims which is prepared by blending an aqueous solution of at least one water-soluble hydroxyalkyl cellulose or of a water-soluble partially saponified polyvinyl acetate, or of a water-soluble partially etherified derivative of such a partially saponified polyvinyl acetate or of a polyvinyl alcohol, at room temperature, with the pigment, in proportion to provide 5 to 30 percent by weight thereof (calculated on the weight of the pigment) in the dispersion.
- 35   7. A pigment dispersion as claimed in claim 1 and substantially as described in any of the Examples.

KILBURN & STRODE,  
Chartered Patent Agents,  
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.  
—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2,  
from which copies may be obtained.